

PATENT SPECIFICATION

NO DRAWINGS

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International Classification:—C08f. B23p. B29d. D06p.

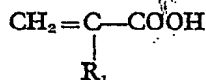
COMPLETE SPECIFICATION

New Copolymers and their manufacture and use

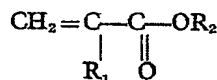
We, CIBA LIMITED, a body corporate organised according to the laws of Switzerland, of Basle, Switzerland, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

It is known to use acrylic resins for the production of coatings and impregnations on fibre-forming and film-forming substances. They have become especially important as binding agents for the production of dyeings or prints with pigments. For this purpose the requirements with regard to the fastness of the dyeings and prints are usually high, so that the dyeings should be of good fastness to rubbing, washing and light. It has been found that in many cases the fastness to washing of such dyeings, when they are exposed to light, is distinctly reduced as compared with the fastness to washing of the unexposed dyeing. For convenience this fastness to washing of an exposed dyeing will be referred to hereinafter as "light-wash fastness".

The present invention is based on the observation that dyeings of improved light-wash fastness can be produced by using as binding agents copolymers obtained from 28—50% of vinylidene chloride, 4 to 10% of an acid of the formula



in which R₁ represents a hydrogen atom or an alkyl group containing 1 to 4 carbon atoms, and at least 35% of an ester of the formula



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in which R₁ has the meaning given above, and —OR₂ represents the residue of an aliphatic, heterocyclic or alicyclic alcohol, and, if desired, a further monomer containing a single ethylenic double bond, the sum of the three first mentioned components amounting to at least 80% by weight of the total monomers.

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Accordingly, this invention provides copolymers as defined above, and their manufacture and use as coating or impregnating agents, and especially as binding agents in dyeing or printing with pigments.

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In each of the foregoing formulae R₁ preferably represents a hydrogen atom or an alkyl group advantageously one containing 1—4 carbon atoms, such as an ethyl or especially a methyl group, and —OR₂ represents the residue of an alcohol of the formula

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This alcohol may be aliphatic or cyclic and it may belong to the heterocyclic or alicyclic series. There may be mentioned, for example, tetrahydrofurfuryl alcohol, cyclohexanol, alkoxy- or alkyl-substituted cyclohexanols, such as ortho-methylcyclohexanol, para-methoxycyclohexanol, and also decahydronaphthols, terpene alcohols such as isoborneol. However, —OR₂ is preferably the residue of a saturated aliphatic alcohol containing 1—18 carbon atoms, of which the alkyl chain may be straight or branched and may be interrupted by ether-

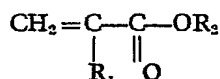
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oxygen atoms. There may be mentioned, for example, methyl alcohol, ethyl alcohol, propyl alcohol, isopropyl alcohol, *n*-butyl-alcohol, isobutyl alcohol, tertiary butyl alcohol, amyl alcohol, 2-ethyl butyl alcohol, *n*-hexyl alcohol, heptyl alcohol, 2-ethyl hexyl-alcohol, dodecyl alcohol, octadecenyl alcohol and octadecyl alcohol, and also methoxy-ethanol, ethoxy-ethanol, butoxy-ethanol and butoxy-butanol.

The esters of the alcohols of the formula HOR₂ are derived from α -alkyl-acrylic acids, such as methacrylic acid, or advantageously from acrylic acid. It will be understood that, instead of a single ester of the above constitution, there may be used mixtures of such esters having different alcohol and/or acid residues. Thus, for example, a mixture of methacrylic acid cyclohexyl ester and ethyl acrylate may be used or a mixture of acrylic acid isobornyl ester with *n*-hexyl methacrylate. Especially advantageous are the esters of the formula



in which R₁ represents a hydrogen atom or a methyl group, and R₂ represents an alkyl group containing 3—7 carbon atoms; thus, for example, acrylic acid *n*-butyl ester or isobutyl ester.

As the further monomers containing a single ethylene double bond, and which may be used in a proportion of up to 20% by weight of the total monomers, there may be mentioned acrylonitrile, methacrylonitrile, styrene, vinyl chloride, chloro-trifluoroethylene, 1:1-difluoroethylene, acrylic acid amide or methacrylic acid amide and derivatives of these amides substituted at the nitrogen atom by at least one radical containing 1—8 carbon atoms, such as *N*-diethyl-acrylic acid amide, *N*-propyl acrylic acid amide, *N*-di-*n*-butyl-acrylic acid amide or tertiary butyl-acrylic acid amide, and also vinyl alkyl ethers containing about 2—10 carbon atoms in the alkyl group, such as vinyl ethyl ether, vinyl, butyl ether, vinyl 2-ethyl-butyl ether or vinyl 2-ethyl-hexyl ether, or vinyl esters of aliphatic carboxylic acids containing 2—4 carbon atoms, such as vinyl acetate. When a component is used which itself yields a hard polymer, for example, acrylonitrile, it is of advantage to use a proportion of vinylidene chloride near the lower end of the said range of proportions.

The copolymers may be made in bulk. However, it is of advantage to carry out the polymerisation in solution or especially in emulsion. Emulsion polymerisation has the great advantage that polymers produced in this manner can be made into coating or impregnating compositions that are easy to apply. The emulsion polymerisation is advantageously carried out with the aid of catalyst and in the presence of an emulsifying agent.

As emulsifying agents for preparing the emulsions of the starting materials there are used those possessing an adequate stability in acid media, for example, fatty alcohol acid sulphuric acid esters, sulphonated castor oil, alkyl sulphonates or oxyalkyl sulphonates containing 12 to 30 carbon atoms, and especially sodium α -oxyoctadecane sulphonate, which is advantageously free from other salts; sulphodicarboxylic acid esters, for example, the sodium salt of sulphosuccinic acid diethyl ester; alkyl-aryl sulphonates the aliphatic part of which contains at least 8 carbon atoms; and also polyglycol ethers of fatty alcohols of high molecular weight containing 12 to 30 carbon atoms, such as cetyl alcohol, oleyl alcohol or octadecyl alcohol, for example, reaction products of 15—30 mols of ethyleneoxide per mol of fatty alcohol. There may also be used emulsifying agents having a pronounced wetting action, such as octyl-phenol polyglycol ethers and acid sulphuric acid esters thereof, and also dodecyl alcohol poly glycol ethers. There may also be used mixtures of such emulsifying agents, or mixtures of such emulsifying agents with protective colloids, such as esters of alginic acid, poly-vinyl alcohols, partially hydrolysed polyvinyl esters, proteins, starches or starch derivatives. However, it is preferable not to add such protective colloids, as their presence generally impairs the film-forming properties of the co-polymers.

As polymerisation catalysts for carrying out the polymerisation there may be used the customary compounds that catalyse polymerisations, such as organic or inorganic peroxides or per-salts, for example, peracetic acid, acetyl peroxide, benzoyl peroxide, benzoyl acetyl peroxide, lauryl peroxide, hydrogen peroxide, percarbonates, persulphates or perborates. As is known, the proportion of catalyst depends on the course of reaction desired or on the properties desired in the copolymer. If desired, two or more agents that catalyse the polymerisation may be used. The action of the polymerisation catalyst may be increased by the action of heat and/or actinic rays. In some cases it may be possible to carry out the polymerisation with the aid of heat and/or actinic rays alone, that is to say, without the addition of a catalyst.

For producing artificial resin emulsions in accordance with the invention the customary apparatus may be used, and they may be prepared in two stages. In the first stage the emulsion of the starting material may be formed and polymerisation carried out in the second stage. Since the acids to be copolymerised, for example, acrylic acid or methacrylic acid are soluble in water, these acids may be dissolved in the water which contains the emulsifying agent and, if desired, other additions, before the emulsion is prepared. Alternatively, these acids may be mixed with a previously prepared emulsion of the other

components.

For emulsifying the components that are sparingly soluble in water a mixture of these components may be prepared and the mixture subsequently emulsified. Alternatively, one of the components may be emulsified alone and then the remaining components may be dispersed in the emulsion so obtained. Another alternative is to prepare separate emulsions of the several components and to mix the emulsions together in appropriate relative proportions before the polymerisation. Finally, the following procedure may be used:

All except one of the components are emulsified in a single emulsion, and a separate emulsion is prepared with the remaining component, and the latter emulsion is added to the first mentioned emulsion during the polymerisation. This procedure may be of advantage when one of the components polymerises more rapidly and easily than the other components. Advantageously the emulsion polymerisation is carried out with the use of the several components in the monomeric state. Alternatively, one or other of the components may be used in a partially prepolymerised state. The emulsions used for the polymerisation are all those wherein the water is the dispersion medium and the polymer is the disperse phase.

The polymerisation may be carried out at ordinary temperature, but is advantageously carried out at a raised temperature. Suitable temperatures are, for example, within the range of 40° C.—95° C, and especially 55° C.—90° C. In carrying out these polymerisations there is often a considerable liberation of heat, so that they must be carried out with the use of cooling means in order to maintain the desired polymerisation temperature. This is especially necessary when a large quantity of emulsion is polymerised in one operation. In order to utilise the heat liberated and to control the polymerisation temperature more easily, it is of advantage to place in the polymerisation apparatus a small part of the total quantity of emulsion to be treated and to initiate the polymerisation in this part of the emulsion. When a certain temperature is reached in this part of the emulsion, for example, 60—70° C, the remainder of the cold emulsion may be run in in such manner as to keep the temperature constant. Towards the end of the polymerisation it is often necessary to supply heat externally.

As stated above, the polymerisation depends on the nature and proportion of the polymerisation catalyst, which is generally added to the emulsion just before the beginning of the polymerisation in order to control the speed of reaction and the molecular weight of the copolymer produced, so-called regulators, for example, mercaptans may be added.

It is also of advantage to carry out the polymerisation in the absence of air or oxygen and in the presence of an inert gas such as nitrogen

or carbon dioxide. Moreover, in addition to catalysts and regulators, there may be used so-called activators. Such activators are, for example, inorganic oxidisable oxygen-containing sulphur compounds, such as sulphur dioxide, sodium bisulphate, sodium sulphite, ammonium bisulphite, sodium hydrosulphite or sodium thiosulphate. When such an activator is present together with a polymerisation catalyst that yields oxygen a so-called redox system is formed which favourably influences the course of the polymerisation. As activators there may be used water-soluble aliphatic tertiary amines, such as triethanolamine or diethyl-ethanolamine. The action of the polymerisation catalyst may also be accelerated by the addition of a heavy metal compound capable of existing in more than one valency state and which is present in reduced condition, or by the addition of a complex cyanide of iron, cobalt, molybdenum, mercury, zinc, copper or silver or a mixture of such complexes.

The process for the manufacture of the copolymers of this invention may be carried out in a continuous manner, although it is preferably carried out in a discontinuous manner.

The dispersions of copolymers of this invention have an acid reaction and are generally thinly liquid. Dispersions of suitable concentration can be converted by complete or partial neutralisation, advantageously with the use of a concentrated aqueous solution of ammonia, into salve-like or pasty masses.

The new copolymer emulsions are very stable whether they are acid or alkaline, and can therefore be applied in the thinly liquid state or in a salve-like or pasty condition. A wide range of organic or inorganic pigments or fillers may be incorporated with the dispersions. When such pigments or fillers are used, the dispersion can be thickened after the addition of the pigment or filler, which facilitates the use of the emulsion and widens its range of applications. Other modifying substances may be added, such as plasticisers, for example, dibutyl phthalate or dioctyl phthalate, or sebacic acid esters.

The products of this invention are principally suitable for the production of elastic coatings of good adhesion on fabrics of all kinds, for example, fabrics of cotton, jute, hemp, straw, polyesters, artificial or natural silk, staple fibres of regenerated cellulose, polyamides, polyacrylo-nitrile or glass. These dispersions may, if desired, be thickened with ammonia and then spread on such a fabric or on paper by means of a doctor spreading machine. In this manner it is possible to manufacture with the new products, for example, water-resistant raincoat materials, imitation wax or oil cloth, tent material, oiled silk material and rear dressings on corduroy or carpets. Owing to their good adhesion the copolymers are also suitable as backing layers under polyvinyl chloride coatings, for example,

for the production of artificial leather, and also as binding agents for colouring compositions applied to leather.

5 The dispersions of this invention can also be used unthickened for production by the immersion method of filling dressings on fabrics of all kinds. In this manner there can be produced, for example, bed ticking material, cloths having feel-modifying dressings that are resistant to washing, water-resistant tent materials and lining materials that are resistant to dry cleaning and are not brittle. Other uses for the new products are for adhesively uniting foils of polyvinyl chloride or other synthetic resins, and for adhesively uniting paper or metal sheets to one another or paper sheets to metal sheets, or for coating glass fabrics or cloth fabrics of all kinds.

20 As mentioned above, the copolymers of this invention are especially suitable as binding agents for pigment dyeing or printing on textile materials of all kinds.

25 The fibrous materials to be treated are more especially fabrics of natural or regenerated cellulose such as cotton, linen, artificial silk or staple fibres of regenerated cellulose, or cellulose esters such as cellulose acetate silk, wool, silk or synthetic fibrous materials such as polyamide, polyester or polyacrylonitrile fibres, or glass fibres. There are also suitable textile materials composed of mixtures of the foregoing fibres.

30 Application No. 19389/59 (Serial No. 908,223), describes and claims a process for improving materials in the form of fibres or films, the aqueous dispersions employed in that process and the concentrated preparations for making the dispersions. It is known from that application to use the copolymers of the present invention in combination with an aqueous dispersion of a water-insoluble derivative of a formaldehyde condensation product of an amino compound capable of forming a hardenable resin with formaldehyde and/or a water-soluble formaldehyde condensation product of an amino compound capable of forming a hardenable resin with formaldehyde or a water-soluble ether of such condensation product and to dry the material and to harden the impregnation or coating at a raised temperature.

50 The following Examples illustrate the invention, the parts and percentages being by weight unless otherwise specified and the relation between parts by weight and parts by volume being the same as that between the litre and the kilogram:

EXAMPLE 1

60 A solution of 3.6 parts of sodium α -hydroxy-octadecanesulphonate in 150 parts of water is mixed with 72 parts of isobutylacrylate, 42 parts of vinylidene chloride and 6 parts of acrylic acid. 0.4 part of triethanolamine and 0.2 part of isooctanol are further added, the whole is intimately mixed and one half of the mixture is introduced into a stirred vessel of

a capacity of 500 parts by volume which is equipped with a thermometer and a reflux condenser cooled by means of ice water. Before charging it with the emulsion, the whole apparatus is thoroughly swept with nitrogen.

70 The emulsion is heated to an internal temperature of 60° C, and a solution of 0.06 part of potassium persulphate in 6 parts of water is added. After about 15 minutes the temperature rises slightly, whereupon the remainder of the emulsion described above is added dropwise within 1 hour, after it has been treated with a solution of 0.06 part of potassium persulphate in 6 parts of water. 15 minutes after completion of the dropwise addition the temperature has risen to about 66° C; another solution of 0.06 part of potassium persulphate in 6 parts of water is added, which causes another rise of the temperature to about 71° C. At intervals of 2 hours each another two additions of 0.06 part of potassium persulphate in 6 parts of water each are made, and after the last addition the internal temperature is raised by 10° C. and 2 hours later the whole is cooled to room temperature.

A very finely dispersed, syrupy emulsion containing about 40% of resin is obtained. The yield of polymer amounts to 93 to 95% of the theoretical.

EXAMPLE 2

95 A solution of 3.6 parts of sodium α -hydroxy-octadecanesulphonate in 150 parts of water is mixed with 78 parts of isobutylacrylate, 36 parts of vinylidene chloride and 6 parts of acrylic acid. 0.4 part of triethanolamine and 0.2 part of isooctanol are further added, and the whole is intimately mixed and further processed as described in Example 1.

100 A very finely dispersed, syrupy emulsion containing about 40% of resin is obtained. The yield of polymer amounts to about 93% of the theoretical.

EXAMPLE 3

110 A solution of 9 parts of sodium α -hydroxy-octadecane-sulphonate in 280 parts of water is mixed with 180 parts of isobutylacrylate, 105 parts of vinylidene chloride and 15 parts of acrylic acid. 1 part of triethanolamine and 0.6 part of isooctanol are further added, the whole is intimately mixed and one half of this emulsion is introduced into a stirred vessel of 1000 parts by volume capacity which is equipped with a thermometer and a reflux condenser cooled with ice water. Before charging it with the emulsion, the whole apparatus is thoroughly swept with nitrogen.

120 The emulsion is heated to an internal temperature of 60° C. and a solution of 0.12 part of potassium persulphate in 2.4 parts of water is then added. After about 15 minutes the temperature has risen by about 5° C, and 1 hour later the remainder of the emulsion described above is added dropwise after having been treated with a solution of 0.12 part of potassium persulphate in 2.4 parts of water. 20

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minutes after completion of the dropwise addition the temperature has risen by 6°C; another solution of 0.12 part of potassium persulphate in 2.4 parts of water is added, whereupon the temperature rises again to about 75° C. At intervals of 2 hours each two more additions of 0.12 part of potassium persulphate in 2.4 parts of water each are made. After the last addition the internal temperature is raised by 10° C. and 2 hours later the whole is cooled to room temperature.

A very finely dispersed, thinly liquid emulsion is obtained which contains about 50% of resin. The yield of polymer amounts to about 98% of the theoretical.

EXAMPLE 4

A solution of 4.5 parts of sodium α -hydroxy-octadecanesulphonate in 140 parts of water is mixed with 82.5 parts of isobutylacrylate, 60 parts of vinylidene chloride and 6 parts of acrylic acid. 0.5 part of triethanolamine and 0.3 part of isooctanol are further added, the whole is intimately mixed, and one half of this emulsion is introduced into a stirred vessel of 500 parts by volume capacity which is equipped with a thermometer and a reflux condenser cooled with ice water. Before being charged with the emulsion, the whole apparatus is thoroughly swept with nitrogen.

The emulsion is raised to an internal temperature of 57° C, and a solution of 0.06 part of potassium persulphate in 1.2 parts of water is added. After about 15 minutes the temperature rises slightly by 3 to 4° C, whereupon in the course of 1 hour the remainder of the emulsion described above is added dropwise after having been treated with a solution of 0.06 part of potassium persulphate in 1.2 parts of water. 20 minutes after completion of the dropwise addition the temperature has risen to about 68° C. Another solution of 0.06 part of potassium persulphate in 1.2 parts of water is then added, whereupon the temperature rises to about 72° C. At intervals of 2 hours each another two additions of 0.06 part of potassium persulphate in 1.2 parts of water each are made; after the last addition the internal temperature is raised by 10° C. and 2 hours later the whole is cooled to room temperature.

A very finely dispersed, thinly syrupy emulsion is obtained which contains about 50% of resin. The yield of polymer amounts to 93 to 94% of the theoretical.

EXAMPLE 5

When in the emulsion described in Example 4 the isobutylacrylate is replaced by an equal amount of *n*-butylacrylate, proceeding otherwise exactly as described, a finely dispersed, syrupy emulsion of about 50% resin content is likewise obtained. The yield of polymer amounts to about 94% of the theoretical.

EXAMPLE 6

When in the emulsion described in Example 4 the isobutylacrylate is replaced by an equal amount of 2-ethylbutylacrylate, proceeding

otherwise in identical manner, a finely dispersed, syrupy emulsion of about 50% resin content is likewise obtained. The yield of polymer amounts to 92 to 93% of the theoretical.

EXAMPLE 7

When in the emulsion described in Example 4 the mixture of monomers is replaced by a mixture of 67.5 parts of 2-ethylbutylacrylate, 75 parts of vinylidene chloride and 7.5 parts of acrylic acid, proceeding otherwise in identical manner, a finely dispersed, syrupy emulsion of about 50% resin content is obtained.

EXAMPLE 8

When in the emulsion described in Example 4 the mixture of monomers is replaced by a mixture of 7.5 parts of acrylic acid, 90 parts of *n*-butylmethacrylate and 52.5 parts of vinylidene chloride, proceeding otherwise in identical manner, a finely dispersed, syrupy emulsion of about 50% resin content is obtained.

EXAMPLE 9

When in the emulsion described in Example 4 the mixture of monomers is replaced by a mixture of 7.5 parts of methacrylic acid, 90.0 parts of *n*-butylacrylate and 52.5 parts of vinylidene chloride, proceeding otherwise in identical manner, a finely dispersed, syrupy emulsion is obtained which has a resin content of about 50%.

EXAMPLE 10

When in the emulsion described in Example 4 the mixture of monomers is replaced by a mixture of 7.5 parts of acrylic acid, 15 parts of acrylonitrile, 75 parts of *n*-butylacrylate and 52.5 parts of vinylidene chloride, proceeding otherwise in identical manner, a finely dispersed, syrupy emulsion is obtained which has a resin content of about 50%.

EXAMPLE 11

When in the emulsion described in Example 4 the mixture of monomers is replaced by a mixture of 7.5 parts of acrylic acid, 3 parts of acrylonitrile, 87 parts of *n*-butylacrylate and 52.5 parts of vinylidene chloride, proceeding otherwise in identical manner, a finely dispersed, syrupy emulsion is obtained which has a resin content of about 50%.

EXAMPLES 12

When in the emulsion described in Example 4 the mixture of monomers is replaced by a mixture of 7.5 parts of acrylic acid, 7.5 parts of acrylonitrile, 82.5 parts of *n*-butylacrylate and 52.5 parts of vinylidene chloride, proceeding otherwise in identical manner, a finely dispersed, syrupy emulsion is obtained which has a resin content of about 50%.

EXAMPLE 13

When in the emulsion described in Example 4 the mixture of monomers is replaced by a mixture of 7.5 parts of acrylic acid, 22.5 parts of acrylonitrile, 52.5 parts of vinylidene chloride and 67.5 parts of butylacrylate, proceeding otherwise in identical manner, a finely

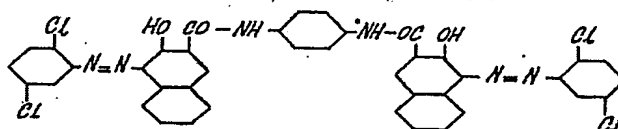
dispersed, syrupy emulsion is obtained which has a resin content of about 50%.

EXAMPLE 14

When in the emulsion described in Example 4 the mixture of monomers is replaced by a mixture of 7.5 parts of acrylic acid, 30 parts of acrylonitrile, 52.6 parts of vinylidene chloride and 60 parts of *n*-butylacrylate, proceeding otherwise in identical manner, a finely dispersed, syrupy emulsion is obtained which has a resin content of about 50%.

EXAMPLE 15

When in the emulsion described in Example 4 the mixture of monomers is replaced by a mixture of 7.5 parts of acrylic acid, 22.5 parts of di-*n*-butylacrylamide, 67.5 parts of vinylidene chloride and 52.5 parts of *n*-butylacrylate, proceeding otherwise in identical manner, a finely dispersed, syrupy emulsion is obtained which has a resin content of about 50%.

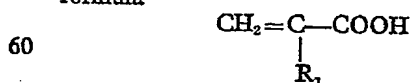


50 Mercerised, bleached cotton poplin is impregnated at room temperature on the padder with one of these dye baths, squeezed to a liquor content of about 60%, dried at 70 to 90° C. and finally hardened for 5 minutes at 160° C.

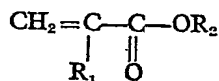
55 The resulting dyeings have good fastness to scrubbing, washing and rubbing. In addition, the dyeings are very fast to washing after having been exposed for 100 hours in a "Fadeometer" (Registered Trade Mark) and then washed at the boil with soap and soda. The fastness to washing is equal to that of the unexposed control dyeing.

WHAT WE CLAIM IS:—

1. Copolymers obtained from 28—50% of vinylidene chloride, 4—10% of an acid of the formula



in which R_1 represents a hydrogen atom or an alkyl group containing 1 to 4 carbon atoms, at least 35% of an ester of the formula



65 in which R_1 has the meaning given above, and — OR_2 represents the residue of an aliphatic, heterocyclic or alicyclic alcohol, and, if desired, a further monomer containing a single ethylenic double bond, the sum of the three first-

EXAMPLE 16

When in the emulsion described in Example 4 the mixture of monomers is replaced by a mixture of 7.5 parts of acrylic acid, 22.5 parts of styrene, 45 parts of vinylidene chloride and 75 parts of *n*-butylacrylate, proceeding otherwise in identical manner, a finely dispersed syrupy emulsion is obtained which has a resin content of about 50%.

EXAMPLE 17

An aqueous dye bath is prepared containing in 1000 parts 55 parts of the emulsion described in Example 1, 40 parts of sodium alginate thickening 30:1000, 5 parts of diammonium phosphate and one of the following aqueous dyestuff pastes:

- 3 parts of a paste containing 15% of copper phthalocyanine
- 11 parts of a paste containing 15% of the azo-pigment of the formula

mentioned components amounting to at least 80% by weight of the total monomers.

2. Copolymers as claimed in claim 1, in which the ester of the second mentioned formula contains as R_1 a hydrogen atom or a methyl group, and as R_2 an alkyl group containing 3—7 carbon atoms.

3. Copolymers as claimed in claim 2, in which the said ester is acrylic acid isobutyl ester.

4. Copolymers as claimed in claim 2, in which the said ester is acrylic acid *n*-butyl ester.

5. Copolymers as claimed in any one of claims 1—4, in which the acid of the first mentioned formula is acrylic acid.

6. An aqueous emulsion of a copolymer claimed in any one of claims 1—5.

7. A copolymer having substantially the constitution of the copolymer obtainable as described in any one of Examples 1—16 herein.

8. An aqueous emulsion of a copolymer obtained substantially as described in any one of Examples 1—16 herein.

9. Coating or impregnating compositions which contain a copolymer claimed in any one of claims 1—5 or 7.

10. Coating or impregnating compositions as claimed in claim 9, which comprise an aqueous emulsion of the copolymer.

11. In the process of pigment-dyeing or pigment printing the improvement which consists in using as binding agent a copolymer claimed in any one of claims 1—5 and 7.

12. A pigment dyeing process using copolymers according to Claim 1 and conducted substantially as described in Example 17 herein.

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